

## **STEAM RECOMPRESSION IN CARBOXYLIC ACID PROCESSES**

### **FIELD OF INVENTION**

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This invention is related to the efficient energy integration within an aromatic carboxylic acid production facility by utilizing the reaction exotherm as a source of energy for a steam heating medium to produce low pressure steam and then subjecting the low pressure steam to a compression zone to form an intermediate pressure steam.

### **BACKGROUND OF THE INVENTION**

15           Aromatic carboxylic acids, such as terephthalic acid, isophthalic acid, and naphthlene dicarboxylic acid are useful chemical compounds and are raw materials in the production of polyesters and copolyesters. In the instance of terephthalic acid, a single manufacturing facility can produce greater than 100,000 metric tons per annum as feedstock for a polyethylene terephthalate (PET) facility.

20           Terephthalic acid (TPA) can be produced by the high pressure, exothermic oxidation of a suitable aromatic feedstock such as para-xylene in a solvent such as acetic acid, water, or mixtures thereof. Typically, these oxidations are carried out in a liquid phase using air or alternate sources of molecular oxygen in the presence of metal catalyst(s) or promoter compound(s). Methods for oxidizing para-xylene and other aromatic

compounds such as m-xylene and dimethylnaphthlene are well known in the art.

In addition to oxidation, many industrial TPA processes also incorporate a hydrotreating (hydrogenation) process to produce a so-called  
5 purified terephthalic acid or PTA. Typically, these processes are conducted using a water solvent. These hydrogenation processes are also well known in the art.

TPA processes give rise to high temperature material streams. These streams are derived from both the heating needs within the process  
10 and heat removal needs. Typical would be to provide some sort of heat input which would result in the boiling or evaporation of a solvent. Energy could then be recovered via condensation of the solvent.

As the art has progressed, a significant body of literature has been developed to address the problem of efficient energy recovery within the  
15 TPA process. In general, these schemes usually involve the recovery of useful work/electricity via the use of a turbine and/or the recovery of heat energy via the use of steam generation. Both of these general schemes have certain drawbacks and limitations.

In the case of recovery of work/electricity via the use of a turbine,  
20 there are significant technical and economic problems. In the case of steam generation, the technical problems of physically producing steam are relatively insignificant. However, the limitations are generally associated with the usefulness of the steam generated. Specifically, the steam

generated from TPA processes generally is at too low a temperature and/or pressure to be useful as a heating medium in general. And specifically within the remainder of the process.

Although, by themselves mechanical energy recovery via a turbine  
5 and heat energy recovery via steam generation are not necessarily novel, the objective of this invention is to describe a method of heat energy recovery involving the generation of steam followed by processing of the generated steam into a more useful form.

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#### **SUMMARY OF THE INVENTION**

Disclosed are various configurations for producing steam in carboxylic acid production processes. Although steam generation within terephthalic acid production processes in itself is well known, this invention  
15 discloses a method for the re-compression of process generated low pressure steam to create an intermediate pressure steam that is useful as a heating medium, specifically in other parts of the terephthalic acid production process or generally utilized in another process. The invention comprises the following basic steps:

- 20       1. Recovering thermal energy in a first heat transfer zone from a high temperature process stream and then using the thermal energy to generate a low pressure steam; wherein the high temperature

material stream is a result of an aromatic carboxylic acid production process;

2. Subjecting the low pressure steam to a compression zone to generate an intermediate pressure steam;
- 5 3. Utilizing the intermediate pressure steam in a second heat transfer zone as a heating media, specifically within other parts of the terephthalic acid (or other aromatic carboxylic acid) process or generally utilized in another process thereby generating steam condensate; and
- 10 4. Optionally, recycling all or part of the steam condensate to the first heat transfer zone for low pressure steam generation.

It is an object of this invention to provide a process to produce an intermediate pressure steam from a high temperature process stream.

- It is another object of this invention to provide a process to recover
- 15 thermal energy from a high temperature process stream wherein the carboxylic acid vapor stream comprising primarily any acetic acid or any solvent in a carboxylic acid production process, water, and mixture thereof.

- It is another object of this invention to provide a process for efficient energy integration within a carboxylic acid production facility by utilizing the
- 20 reaction exotherm from at least one oxidation reaction directly or indirectly as a source of energy for a steam heating medium to produce low pressure steam and then subjecting the low pressure steam to a compression zone to form an intermediate pressure steam.

It is another object of this invention to provide a process for efficient energy integration within the terephthalic acid production facility by utilizing the reaction exotherm from at least one oxidation reaction directly or indirectly as a source of energy for a steam heating medium to produce low  
5 pressure steam and then subjecting the low pressure steam to a compression zone to form an intermediate pressure steam.

In one embodiment of the invention, a process to produce an intermediate pressure steam from a high temperature process stream is  
10 provided. The process comprises:

- (a) recovering thermal energy from at least a portion of the high temperature process stream in a first heat transfer zone to produce a low pressure steam; and
- (b) compressing the low pressure steam in a compression zone  
15 to produce an intermediate pressure steam.

In another embodiment of the invention, a process to recover thermal energy from a high temperature process stream is provided. The process comprises:

- (a) recovering thermal energy from at least a portion of the high  
20 temperature process stream in a first heat transfer zone to produce a low pressure steam;
- (b) compressing the low pressure steam in a compression zone to produce an intermediate pressure steam;

(c) recovering thermal energy from at least a portion of the intermediate pressure steam in a second heat transfer zone to produce steam condensate; and

(d) optionally recycling at least a portion of the steam condensate  
5 to the first heat exchange zone.

In another embodiment of this invention, a process to recover thermal energy from a high temperature process stream is provided. The process comprises:

(a) recovering thermal energy from at least a portion of the high  
10 temperature process stream in a first heat transfer zone to produce a low pressure steam;

(b) compressing the low pressure steam in a compression zone to produce a intermediate pressure steam; wherein the compression zone comprises at least one steam ejector;

(c) recovering thermal energy from at least a portion of the  
15 intermediate pressure steam in a second heat transfer zone to produce steam condensate; and

(d) optionally recycling at least a portion of the steam condensate to the heat exchange zone.

20 In another embodiment of this invention, a process to recover thermal energy from a high temperature process stream is provided. The process comprises:

(a) recovering thermal energy from at least a portion of the high temperature process stream in a first heat transfer zone to produce a low pressure steam;

(b) compressing the low pressure steam in a compression zone  
5 to produce a intermediate pressure steam; wherein the compression zone comprises at least one compressor;

(c) removing at least a portion of superheat resulting from compression from said intermediate pressure steam;

(d) recovering thermal energy from at least a portion of the  
10 intermediate pressure steam in a second heat transfer zone to produce steam condensate; and

(e) optionally recycling at least a portion of the steam condensate to the heat exchange zone.

In another embodiment of this invention, a process to recover  
15 thermal energy from a high temperature process stream is provided. The process comprises:

(a) oxidizing an aromatic feedstock with a reaction mixture in a reaction zone to form an aromatic carboxylic acid-rich stream and a gaseous mixture;

(b) removing in a separation zone a substantial portion of a  
20 solvent from the gaseous mixture to form the high temperature process stream and a solvent rich stream; and

(c) recovering thermal energy from at least a portion of the high temperature process stream in a first heat transfer zone to produce a low pressure steam;

(d) compressing the low pressure steam in a compression zone  
5 to produce an intermediate pressure steam;

(e) recovering thermal energy from at least a portion of the intermediate pressure steam in a second heat transfer zone to produce steam condensate; and

(f) optionally recycling at least a portion of the steam condensate  
10 to the heat exchange zone.

These objects, and other objects, will become more apparent to others with ordinary skill in the art after reading this disclosure.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

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Figure 1 illustrates one embodiment of this invention. A process is provided to recover thermal energy from a high temperature process stream to produce a low pressure steam and then subjecting the low pressure steam to a compression zone to form an intermediate pressure steam.

20 Figure 2 illustrates steam compression using a steam ejector.

Figure 3 illustrates one embodiment of this invention. A process is provided to recover thermal energy from a high temperature process stream to produce a low pressure steam and then subjecting the low pressure



steam to a compression zone to form an intermediate pressure steam;  
wherein the compression zone comprises at least one steam ejector.

Figure 4 illustrates one of many examples of a process for producing  
a high temperature process stream.

5                    **DETAILED DESCRIPTION OF THE INVENTION**

Various embodiments are disclosed for producing steam in  
carboxylic acid production processes. Carboxylic acids include, but are not  
limited to, aromatic carboxylic acids produced via controlled oxidation of an  
10 organic substrate. Such aromatic carboxylic acids include compounds with  
at least one carboxylic acid group attached to a carbon atom that is part of  
an aromatic ring, preferably having at least 6 carbon atoms, even more  
preferably having only carbon atoms. Suitable examples of such aromatic  
rings include, but are not limited to, benzene, biphenyl, terphenyl,  
15 naphthalene, and other carbon-based fused aromatic rings. Examples of  
suitable carboxylic acids include, but are not limited to, terephthalic acid,  
benzoic acid, p-toluic acid, isophthalic acid, trimellitic acid, naphthalene  
dicarboxylic acid, and 2,5-diphenyl-terephthalic acid.

In one embodiment of this invention, a process to recover thermal  
20 energy from a high temperature process stream **10** is provided. The  
process comprises:

Step (a) recovering thermal energy from at least a portion of the high  
temperature process stream **10** in a first heat transfer zone **20** to produce a

low pressure steam **30**. In an embodiment of the invention, the high temperature process stream **10** is partially or fully condensed in a first heat transfer zone **20** which comprises at least one heat transfer device. The heat transfer can be accomplished by any heat transfer devices known in the art such that heat is transferred without combining the high temperature process stream **10** and the water/steam condensate stream **25**. For example, the heat transfer device could be a shell and tube heat exchanger. Heat is transferred to water/steam condensate **25** in the first heat transfer zone **20** allowing the water to vaporize to produce a low pressure steam **30**. The condensed or partially condensed high temperature process stream exit the first heat transfer zone **20** via conduit **28**. Although steam generation via this method is well-known in the art, the usefulness of the steam generated is limited by the choice of the high temperature process stream **10**. In general, it is most desirable to use a high temperature process stream **10** with the highest temperature available. This is because the pressure and temperature of the steam generated is an important factor in the usefulness and efficiency for the purpose of mechanical energy generation and for use as a heating medium.

In general, there are no limitations on the condition or origin of the high temperature process stream **10** in this invention with the exception that the high temperature process stream **10** is at a sufficient inlet temperature to the first heat transfer zone **20** to produce a low pressure steam **30** at or above atmospheric pressure. The high temperature process stream **10** is

at a temperature sufficient to produce steam at a temperature about 100°C to about 140°C. Both the low pressure steam **30** and intermediate pressure steam **50** disclosed in this invention is at saturation or superheated temperatures. Preferably, the high temperature process stream **10** is at a  
5 temperature greater than 100°C.

The high temperature process stream **10** can be any high temperature stream that exists in an aromatic carboxylic acid production process. The high temperature process stream **10** does not necessarily comprise an aromatic carboxylic acid.

10 Examples of suitable high temperature process streams **10** include but are not limited to vapor from an oxidation reactor or high pressure distillation column described in E.P Patent 0734372, herein incorporated by reference, vapor generated by an oxidation reactor or water removal column described in U.S Patents 5,501,521 and 6,504,051, herein  
15 incorporated by reference, vapor generated by the crude TPA crystallizer or purified TPA crystallizer described in U.S Patent 5,723,656, herein incorporated by reference, or vapor generated by purified TPA crystallizers described in U.S Patent 5,567,842, herein incorporated by reference.

The high temperature process stream **10** can be produced by any  
20 aromatic carboxylic acid production process known in the art. For example as shown in Figure 4, in one embodiment of the invention a process for producing the carboxylic acid vapor stream **10** comprises:

Step (i) comprises oxidizing an aromatic feedstock **305** with a reaction mixture **310** in a reaction zone **315** to form an aromatic carboxylic acid-rich stream **320** and a gaseous mixture **325**.

The reaction mixture **310** comprises water, a solvent, a metal  
5 oxidation catalyst and a source of molecular oxygen. The reaction zone **315** comprises at least one oxidation reactor. The oxidizing is completed under reaction conditions which produce the aromatic carboxylic acid-rich stream **320** and the gaseous mixture **325**. Typically, the aromatic carboxylic acid-rich stream **320** is a crude terephthalic acid slurry.

10 Crude terephthalic acid is conventionally made via the liquid phase air oxidation of paraxylene in the presence of a metal oxidation catalyst. Suitable catalysts include, but are not limited to, cobalt, manganese and bromine compounds, which are soluble in the selected solvent. Suitable solvents include, but are not limited to, aliphatic mono-carboxylic acids,  
15 preferably containing 2 to 6 carbon atoms, or benzoic acid and mixtures thereof and mixtures of these compounds with water. Preferably the solvent is acetic acid mixed with water, in a ratio of about 5:1 to about 25:1, preferably between about 10:1 and about 15:1. However, it should be appreciated that other suitable solvents; such as those disclosed herein,  
20 may also be utilized. Conduit **325** contains a gaseous mixture which comprises vaporized solvent, gaseous by-products, nitrogen and unreacted oxygen generated as a result of an exothermic liquid phase oxidation reaction of an aromatic to an aromatic carboxylic acid. Patents disclosing

the production of terephthalic acid such as U.S. Patent 4,158,738 and 3,996,271 are hereby incorporated by reference.

Step (ii) comprises removing in a separation zone **330** a substantial portion of the solvent from the gaseous mixture **325** to form the  
5 high temperature process stream **345** and a solvent rich stream **340**.

The high temperature process stream **345** comprises water, gaseous by-products, and small amounts of solvent. When the solvent is a low molecular weight carboxylic acid solvent, the ratio of water to low molecular weight carboxylic acid solvent is in the range of about 80:20 to about  
10 99.99:0.01 by mass. The gaseous by-products comprise oxygen, oxidation by-products, such as, carbon monoxide and carbon dioxide, and in the instance when air is used as a source of molecular oxygen, nitrogen. At least a portion of the high temperature process stream or all of the high temperature process stream is sent on to a first heat transfer zone via  
15 conduit **345**. The portion of the high temperature process stream **345** that is sent to the first heat transfer zone **20** is shown on figure 1 via conduit **10**.

Typically, the temperature and pressure conditions of the high temperature process stream **345** are in the range of about 130°C to about 260°C and about 3.5 to about 40 barg. Preferably, the temperature and  
20 pressure conditions of the high temperature process stream **345** are in the range of about 90°C to about 200°C and about 4 barg to about 15 barg. Most preferably, the temperature and pressure conditions of the high

temperature process stream **345** are in the range of about 130°C to about 180°C and about 4 barg to about 10 barg.

The gaseous mixture in conduit **325** is directed to the separation zone **330**. Typically, the separation zone **330** comprises a high pressure  
5 distillation column having between about 20 and about 50 theoretical stages and a condenser or plurality of condensers. In the separation zone **330**, the solvent rich stream is recovered via conduit **340**. The purpose of the separation zone **330** is to perform a separation wherein at least a portion of the solvent is recovered and excess water is removed. In general, for the  
10 purposes of optimized energy recovery, there should be minimal pressure reduction between the contents of conduit **325** and conduit **345** since this represents a loss of potentially recoverable energy. Therefore, the separation zone **330** should operate at temperature and pressure conditions at or near that of the gaseous mixture from conduit **325**. At least  
15 a portion or all of the high temperature process stream **345** is sent to a first heat transfer zone, and the rest of the high temperature process stream can be utilized elsewhere within the process for producing the aromatic carboxylic acid.

Step (b) comprises compressing the low pressure steam **30** in a  
20 compression zone **40** to produce an intermediate pressure steam **50**. This step refers to subjecting the low pressure steam **30** to a compression process to generate the intermediate pressure steam **50**. In one

embodiment of the invention the intermediate pressure steam can be at about 50 psig to about 260 psig. Another range can be at about 50 psig to about 100 psig. The compression zone **40** comprises at least one compression device. For example, compression devices can include, but  
5 are not limited to a centrifugal compressor, a positive displacement compressor, and or a steam ejector. The compression device(s) can operate at a temperature and pressure sufficient to produce the intermediate pressure steam. It is desirable to produce steam close to its saturation temperature, owing to the excellent heat transfer properties of  
10 saturated steam. If there is too much superheat in the steam then the heat transfer in the second heat transfer zone will be inefficient. Superheat added by compression device can be removed or desuperheated before the intermediate pressure steam is sent to the second heat transfer zone. Desuperheating is also known as "superheat attemporation" or steam  
15 conditioning. For example, almost all types of desuperheaters operate by introducing a spray of liquid water into the superheated steam stream. This spray vaporizes, thus consuming the superheat to provide the heat of vaporization. Typically, the only difference between the types of desuperheaters is the mechanism in which the water is atomized and mixed  
20 with the steam. An example of a desuperheating device would be a probe-type desuperheater that automatically admits cooling water into the stream in response to a pneumatic control signal. The water enters through a spray bar with atomizing nozzles. Typically the spray bar is perpendicular

to the flow of the steam. Another type of device is an annular desuperheater. Water is introduced into an annular body in the steam pipe which results in intensive turbulence that assists in the atomization of the water. A third common device is the Venturi desuperheater. This device  
5 uses the velocity of the steam through a venturi to assist in the final atomization of the water. The water is introduced in the throat of the venture. Methods for removing superheat are well known in the art.

Table 1 below provides a summary of compression devices and conditions.

10 The compression ratios are calculated using absolute pressure and represent preferred ranges only.

Table 1. Methods of Steam Compression to Higher Pressure

Compression Device	Inlet Conditions	Compression Ratio ( $P_{\text{outlet}}/P_{\text{inlet}}$ )	Outlet Conditions
Centrifugal Compressor	Saturated Steam or Superheated Steam @ $P > 14$ psia	1.5 to 5	Saturated or superheated steam at $P > 29$ psia
Positive Displacement Compressor	Saturated Steam or Superheated heated @ $P > 14$ psia	1.5 to 10	Saturated or superheated steam at $P > 29$ psia
Steam Ejector	Saturated Steam or Superheated heated @ $P > 14$ psia and high pressure motive steam	1.2 to 3	Saturated steam at $P > 29$ psia



In most cases, a simple compression device can be utilized for the direct compression of low pressure steam to an intermediate pressure. However, in the case of a steam ejector, high pressure motive fluid (i.e. high pressure steam) can be used to “mix” high and low pressure steam **30** to generate an intermediate pressure steam **50**. A simplified schematic is shown in Figure 2. Figure 3 shows and embodiment of the invention utilizing the steam ejector. Figure 3 shares all the same process streams as Figure 1 with the exception of conduit **48** and **75** which are the condensed or partially condensed high pressure steam **48** and the condensate **75** that is not optionally recycled back to the first heat transfer zone **20**. The high pressure steam **48** can either be at saturated or superheated temperature. Equipment sizing and motive steam requirements can be calculated by conventional methods known in the art. Examples of such methods can be found in Ryans and Roper, “Process Vacuum System Design and Operation”, McGraw-Hill, 1986.

Step (c) comprises recovering thermal energy from at least a portion of the intermediate pressure steam **50** in a second heat transfer zone **60** to produce steam condensate **70**. This step refers to utilizing the intermediate pressure steam **50** as a heating media within other parts of the process thereby generating steam condensate **70**. In general, there are no limitations for the use of intermediate pressure steam **50** within the TPA process or any carboxylic acid process known in the art. However, the

preferred use for the intermediate pressure steam **50** as a heating medium is for the purpose of evaporation of acetic acid/water mixtures. Conduit **63** and **65** represent a process stream in an aromatic carboxylic acid production process that recovers energy from the intermediate pressure steam **50**. Heat is transferred without combining stream **63** and **50**.  
Examples of possible intermediate pressure steam **50** uses include, but not limited to, an evaporator as described in U.S Patent 4,939,297 herein incorporated by reference, a distillation column reboiler(s) used in conjunction with the process described in U.S patent 4,939,297, an evaporator as described in U.S. Patent 4,356,319 herein incorporated by reference, a preheater as described in U.S Patent 5,961,942 or EP 0734372 herein incorporated by reference, an acetic acid/water separation column reboiler as describe in U.S patent 6,143,926 and U.S patent 5,959,140 herein incorporated by reference . These examples are intended to be a non-inclusive example list.

In addition to the examples provided above, the steam can also be utilized for non-process specific purposes. Examples include, but are not limited to heat tracing, generation of refrigeration, an energy source for heating, ventilation, and air conditioning (HVAC) purposes, and export of intermediate pressure steam to an external user or customer, or process.

Step (d) comprises optionally recycling at least a portion of the steam condensate **70** to the first heat transfer zone **20**. This step refers to

recycling of all or part of the steam condensate **70** to the first heat transfer zone **20** to generate low pressure steam **30**. In general, there are no limitations on the condition of the steam condensate **70** with the exception that it is of sufficient pressure to supply to the heat transfer device that is  
5 utilized in the first heat transfer zone **20**. For example, in nearly all instances, a pump or similar device can be utilized to provide sufficient pressure.

In the embodiment where the compression zone **40** comprises at least one steam ejector is shown in Figure 3. High pressure steam is sent  
10 into the steam ejector via conduit **48**. In addition, the excess condensate is taken off via conduit **75**.